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X-ray absorption spectroscopy and x-ray magnetic circular dichroism of epitaxially grown Heusler alloy Co$_2$MnSi ultrathin films facing a MgO barrier

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We element specifically studied the electronic and magnetic states of epitaxially grown full-Heusler alloy Co$_2$MnSi (CMS) 1.1 nm (4 ML) thick ultrathin films facing an epitaxial MgO(001) tunnel barrier by means of x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD). *In situ* reflection high-energy electron-diffraction observations indicated that the CMS films grew into the $L2_1$ structure. The observed XAS and XMCD spectra revealed that the CMS ultrathin film was not oxidized. The ratio of Mn and Co spin magnetic moments obtained by applying the sum rules was about 2.7, close to a theoretical value of 2.8 for CMS with the $L2_1$ structure. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2824856]

Co-based full-Heusler alloys (Co$_2$YZ) have attracted much interest as a desirable ferromagnetic electrode material for spintronic devices.[1–5] This is because of their potentially high spin polarization arising from the half-metallic ferromagnetic nature theoretically predicted for some of these alloys, and because of their high Curie temperatures, which are well above room temperature (RT). Some of the present authors recently developed fully epitaxial magnetic tunnel junctions (MTJs) with a Co$_2$YZ thin film of Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al (CCFA), Co$_2$MnSi (CMS), or Co$_2$MnGe as a lower electrode and a MgO(001) tunnel barrier,[3–5] and demonstrated relatively high tunnel magnetoresistance (TMR) ratios of 109% at RT (317% at 4.2 K) for CCFA/MgO/Co$_{50}$Fe$_{50}$ MTJs (Ref. 4) and 90% at RT (192% at 4.2 K) for CMS/MgO/Co$_{50}$Fe$_{50}$ MTJs.[3] The electronic and magnetic states of the interfacial region of ferromagnetic electrodes with a tunnel barrier play an essential role in the spin-dependent tunneling characteristics in MTJs. It has recently been shown that x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements are powerful techniques for obtaining microscopic information about the element-specific electronic and magnetic states in the interfacial region of MTJs.[6–9]

Our purpose of the present study is to clarify the electronic and magnetic states of the interfacial region of Co$_2$YZ thin films facing a MgO barrier. For this study, we fabricated epitaxial CMS ultrathin films as typical Co$_2$YZ films with an epitaxial MgO barrier and performed XAS and XMCD measurements at the Mn-$L_{2,3}$ and Co-$L_{2,3}$ edges. To investigate the interfacial region selectively, we fabricated CMS ultrathin films with a 4 ML thickness (=1.1 nm). The fabricated sample layer structure (from the substrate side) was as follows: MgO buffer (10 nm)/Fe underlayer (50 nm)/CMS ul-

trathin film (1.1 nm=4 ML)/MgO barrier (2 nm)/Ru cap (2 nm) (hereafter called Fe/CMS (4 ML)/MgO), grown on a MgO(001) single-crystal substrate. The monolayer of Co$_2$MnSi consists of a Co plane and a Mn–Si plane, and a unit cell of CMS, whose lattice parameter is 0.5654 nm (Ref. 10), corresponds to 2 ML of CMS. To stabilize the ferromagnetism of ultrathin CMS films at RT, we grew them on the Fe underlayer. Each layer in the sample layer structure was successively deposited in an ultrahigh vacuum chamber (base pressure: about 6×10^{-8} Pa) through the combined use of magnetron sputtering for Fe, CMS, and Ru, and electron beam evaporation for MgO; the fabrication procedure was the same as in previous work.[3–5] The Fe layer was deposited at RT on the MgO buffer layer, and subsequently annealed *in situ* at 400 °C. The CMS film deposited at RT was subsequently annealed *in situ* at 325 °C for 15 min. To ensure no Fe diffusion into the ultrathin CMS film, we used a relatively low annealing temperature of 325 °C based on Ref. 11. Although we did not confirm directly the suppression of Fe diffusion into the CMS films annealed at 325 °C, no signature of Fe diffusion was suggested in the structural or XAS/XMCD evaluations throughout the present study. The pressure during the deposition of the MgO barrier was about 6×10^{-7} Pa. The film composition for CMS films used in this study was estimated to be Co$_2$Mn$_{0.91}$Si$_{0.93}$ according to inductively coupled plasma analysis results. As a reference sample, we prepared the same layer structure except that the CMS (4 ML) film was intentionally oxidized by exposing it to an O$_2$ atmosphere ($\sim 10^5$ Pa) for 120 min (we refer to this sample as Fe/intentionally oxidized CMS (4 ML)/MgO).

Figure 1 shows reflection high-energy electron-diffraction (RHEED) patterns, along the azimuth of $[100]_{\text{MgO substrate}}$ (corresponding to $[110]_{\text{CMS}}$), obtained *in situ* for each successive layer in the Fe/CMS (4 ML)/MgO layer structure during fabrication. From these RHEED observations, we confirmed that all the layers in the Fe/CMS (4 ML)/MgO grew epitaxially with the (001) basal plane.

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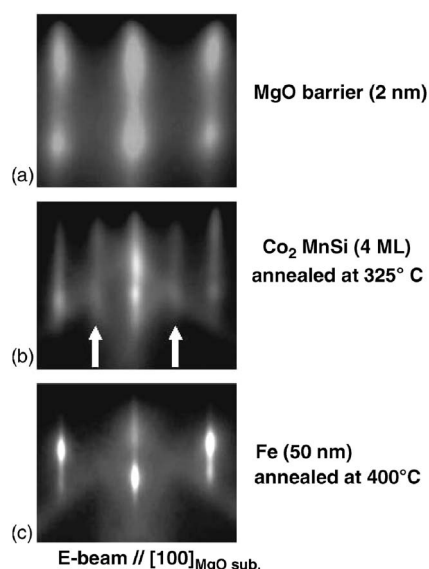
FIG. 1. RHEED patterns, along the azimuth of $[100]_{MgO\ substrate}$ (corresponding to $[110]_{CMS}$), obtained *in situ* for each successive layer in the Fe/CMS (4 ML)/MgO layer structure: (a) an Fe underlayer (50 nm) annealed at 400 °C after deposition; (b) a 4 ML (1.1 nm) Co_2MnSi film annealed at 325 °C after deposition; (c) a MgO barrier (2 nm). In (b), 1/2 order superlattice reflections along the $[110]_{CMS}$ direction (arrows) indicate that the CMS 4 ML film annealed at 325 °C grew into the $L2_1$ structure.

Furthermore, we observed 1/2 order superlattice reflections along the $[110]_{CMS}$ direction in the RHEED patterns for the 4 ML CMS film annealed at 325 °C [Fig. 1(b)], indicating that the CMS film had the $L2_1$ structure.

XAS and XMCD spectra were measured with the total electron yield method using circularly polarized synchrotron radiation at the KEK Photon Factory (BL-11A). The measurements were done at RT. Two XAS spectra for opposite magnetic-field directions (the direction of the magnetic field determines the $3d$ majority-spin direction) were taken consecutively with the photon helicity fixed. XMCD is defined as the difference between the two spectra with the photon helicity parallel (μ_+) and antiparallel (μ_-) relative to the $3d$ majority-spin directions. A magnetic field B (± 3 T) strong enough to saturate the sample magnetization was applied perpendicular to the film surface using a superconducting magnet. The degree of circular polarization of incident light was set to 87% ($\pm 4\%$).

Figures 2(a) and 2(b) show XAS and XMCD spectra at the Mn-$L_{2,3}$ and Co-$L_{2,3}$ edges, respectively, for Fe/CMS (4 ML)/MgO. A small shoulder appeared at the higher photon energy (about 3 eV) side of the Co L_3 peak of the XAS spectrum and a doublet structure appeared in the Mn L_2 region in the XAS spectrum. These two features are typical of those for bulk samples or thin films of Co_2MnZ (Z=Si,Ge).[6,9,12] In particular, a shoulder in the Co XAS spectrum has been commonly observed for bulk samples[12,13] or thin films[6,9] of Co_2YZ with the $L2_1$ structure.

Figures 3(a) and 3(b) show XAS and XMCD spectra at the Mn-$L_{2,3}$ and Co-$L_{2,3}$ edges, respectively, for Fe/ intentionally oxidized CMS (4 ML)/MgO. Comparing the spectra in Fig. 3(a) with those in Fig. 2(a), one can clearly find changes in the Mn-edge XAS and XMCD spectra; the XAS spectrum at the Mn-$L_{2,3}$ edges in Fig. 3(a) exhibits distinct multiplet peaks caused by the oxygen exposure. The multiplet structure is very similar to that in the cal-
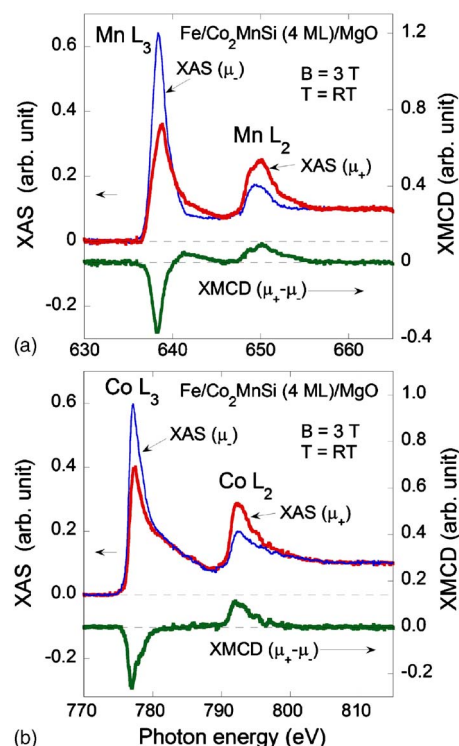

FIG. 2. (Color online) XAS and XMCD spectra at the $L_{3,2}$ edges of (a) Mn and (b) Co atoms in fully epitaxial Fe (50 nm)/CMS (4 ML=1.1 nm)/ MgO barrier (2 nm).

culated XAS spectrum[14] as shown in the inset of Fig. 3(a). The atomic calculation was made for a Mn^{2+} ion with the $3d^5$ electronic configuration assuming a high spin state ($^6S_{5/2}$ ground state)[14] [inset of Fig. 3(a)]. Therefore, we conclude that MnO was formed in the intentionally oxidized CMS (4 ML) thin film. In addition, the XMCD signals at the Mn edges almost completely vanished [Fig. 3(a)], which strongly indicates that the MnO is paramagnetic at RT.

On the other hand, no such multiplet structure appeared in the XAS and XMCD spectra around the Co-$L_{2,3}$ edges for the intentionally oxidized CMS (4 ML) film [Fig. 3(b)]. However, the shoulder at the L_3 peak in the Co-edge XAS spectrum characteristic of full-Heusler alloys with the $L2_1$ structure disappeared, resulting in a Co-edge XAS L_3 peak slightly narrower in the intentionally oxidized CMS (4 ML) film than that in the CMS (4 ML) film [Fig. 2(b)]. Since the XAS spectrum of CoO_x exhibited a typical multiplet structure as observed in the MgO substrate/CoO/Fe layer structure [inset of Fig. 3(b)][15] and in the intentionally oxidized 1 ML Co facing an AlO_x barrier,[16,17] the absence of the multiplet structure in the Co-edge XAS and XMCD spectra indicates that no Co oxide existed in the intentionally oxidized CMS (4 ML) film. The narrower L_3 peak in the Co XAS spectrum for the intentionally oxidized CMS (4 ML) film [Fig. 3(b)], however, should be associated with changes in the electronic band structure due to the formation of MnO in the CMS film. Similar XAS spectra indicating the oxidation of Mn atoms and the absence of the oxidation of Co atoms have been reported for the interface between CMS and an AlO_x barrier.[6,9] One possible reason for the oxidation of Mn atoms and the absence of the oxidation of Co atoms is a higher formation enthalpy of MnO (-86 kcal/mol) compared with that of CoO (-51 kcal/mol).[9,18]
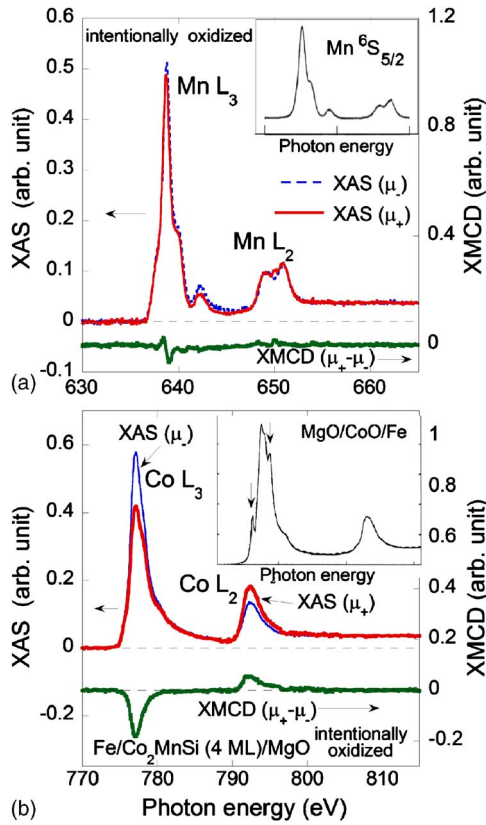
FIG. 3. (Color online) XAS and XMCD spectra at the $L_{3,2}$ edges of (a) Mn and (b) Co atoms in Fe (50 nm)/intentionally oxidized CMS (4 ML=1.1 nm)/MgO barrier (2 nm). The inset of (a) shows the theoretically calculated XAS spectrum for the atomic Mn $3d^5$ electronic configuration ($^6S_{3/2}$ ground state) (Ref. 14). The inset in (b) shows a XAS spectrum for Co atom in the sandwich structure of MgO substrate/CoO/Fe (Ref. 15).

Magnetic moments of Mn and Co atoms are obtained by applying the sum rules.[19] The orbital (m_{orb}) and spin (m_{spin}) magnetic moments are given separately as follows:

$$m_{orb} = -\frac{4}{3}\frac{q}{r}n_h\mu_B, \tag{1}$$

$$m_{spin} + 7m_T^z = -\frac{6p-4q}{r}n_h\mu_B, \tag{2}$$

where r is the XAS energy integral, $r=\int_{L_3+L_2}(\mu_++\mu_-)d\omega$, q is the XMCD energy integral over the $L_{2,3}$ edges, and $q=\int_{L_3+L_2}(\mu_+-\mu_-)d\omega$. p is the XMCD energy integral over the L_3 edge, expressed as $p=\int_{L_3}(\mu_+-\mu_-)d\omega$, and $m_T^z=\langle T_z\rangle\mu_B/\hbar$ with $\langle T_z\rangle$ being the expectation value of the intra-atomic magnetic dipole operator.[19] For the evaluation of m_{spin} and m_{orb} for the CMS films facing a MgO barrier, we assumed a $3d$ hole number n_h of 4.52 for Mn and 2.24 for Co based on a band structure calculation[20] and ignored the $\langle T_z\rangle$ value, assuming the term to be very small. The m_{spin} of Mn atoms thus obtained should be corrected for the effect of the jj mixing arising from $2p$-$3d$ electrostatic interaction.[6,21] However, we estimated the m_{spin} of Mn atoms using the bare spin sum rule because a correction factor for Mn atoms in CMS with the $L2_1$ structure is not accurately known. The obtained m_{spin} values for Co and Mn atoms were 1.25 ± 0.1 and $3.35\pm0.1\mu_B$, respectively, for CMS (4 ML). Both values are about 15% larger than the theoretically obtained ones of 1.06 and $2.92\mu_B$ for bulk CMS with the $L2_1$ structure.[22] In

addition to systematic error in the sum-rule analysis, some structural disorder may exist in the 4-ML-thick CMS film. The m_{spin} ratio of 2.7 for Mn and Co atoms in the present work is, however, close to a theoretically calculated value of 2.8 (Ref. 22), indicating that the 4-ML-thick CMS film in the present work still maintained the $L2_1$ structure. The *in situ* RHEED observations also indicated the $L2_1$ structure for our 4 ML CMS films. The obtained m_{orb} values of Co and Mn atoms were 0.06 ± 0.1 and $0.05\pm0.1\mu_B$, respectively, which are very small. These small m_{orb} values indicate a quenching of the orbital magnetic moment due to the cubic symmetry.[22]

In summary, the XAS and XMCD spectra observed at the Mn-$L_{2,3}$ and Co-$L_{2,3}$ edges in fully epitaxial layer structures of Fe underlayer/CMS ultrathin film (4 ML)/MgO barrier directly revealed that the interfacial region of the CMS film facing a MgO barrier was not oxidized. The ratio of 2.7 for the Mn and Co spin magnetic moments obtained through the sum-rule analyses is close to the theoretical value of 2.8 for CMS with the $L2_1$ structure. The *in situ* RHEED observations also indicated the $L2_1$ structure for our 4 ML CMS films. These results distinctly show a high-quality interface in CMS films facing a MgO barrier in terms of electronic and magnetic states.

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